Concentration and δD of molecular hydrogen in boreal forests: Ecosystem-scale systematics of atmospheric H_2

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[1] We examined the concentration and δD of atmospheric H_2 in a boreal forest in interior Alaska to investigate the systematics of high latitude soil uptake at ecosystem scale. Samples collected during nighttime inversions exhibited vigorous H_2 uptake, with concentration negatively correlated with the concentration of CO_2 (-0.8 to -1.2 ppb H_2 per ppm CO_2) and negatively correlated with δD of H_2. We derived H_2 deposition rates of between 2 to 12 nmol m^{-2} s^{-1}. These rates are comparable to those observed in lower latitude ecosystems. We also derive an average fractionation factor, $\alpha = D{:}H_{residual}/D{:}H_{consumed} = 0.94 \pm 0.01$ and suggestive evidence that α depends on forest maturity. Our results show that high northern latitude soils are a significant sink of molecular hydrogen indicating that the record of atmospheric H_2 may be sensitive to changes in climate and land use. *INDEX TERMS:* 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1615 Global Change: Biogeochemical processes (4805); 1040 Geochemistry: Isotopic composition/chemistry. **Citation:** Rahn, T., J. M. Eiler, N. Kitchen, J. E. Fessenden, and J. T. Randerson, Concentration and δD of molecular hydrogen in boreal forests: Ecosystem-scale systematics of atmospheric H_2, *Geophys. Res. Lett.*, *29*(18), 1888, doi:10.1029/2002GL015118, 2002.

1. Introduction

[2] Molecular hydrogen (H_2) is the second most abundant reduced gas in the atmosphere (after methane) with a globally averaged mixing ratio of ~530 ppbv [*Novelli et al.*, 1999]. Its largest source is believed to be photochemical oxidation of methane and non-methane hydrocarbons; other recognized sources include biomass burning, fossil fuel burning, and ocean degassing. Hydrogen is unusual for a trace gas with anthropogenic sources in that the concentration in the southern hemisphere is greater (by ~3%, relative) than that in the northern hemisphere; furthermore, seasonal amplitudes increase with latitude in the northern hemisphere. Combined, these observations indicate that land surface in the northern hemisphere is an important sink of atmospheric H_2. Oxidation by OH radicals is the final recognized component of the H_2 budget.

[3] The budget and spatial and temporal distribution of atmospheric H_2 suggest that it is a unique tracer of the interplay of processes relating climate and land use change. Previous studies have examined the uptake of H_2 in flux chamber experiments on tropical and temperate soils [*Seiler*, 1978; *Conrad and Seiler*, 1985; *Yonemura et al.*, 1999; *Yonemura et al.*, 2000a; *Yonemura et al.*, 2000b], and the isotopic effects associated with that uptake [*Ehhalt et al.*, 1989; *Gerst and Quay*, 2001]. However, there are no prior observations of ecosystem-wide rates and isotopic systematics of H_2 uptake by soils, and no observations of any type of soils from high northern latitudes. We report here the results of a study of the concentration and stable isotope systematics of H_2 in interior Alaskan boreal forests during July of 2001. This study is one in a series examining the atmospheric H_2 budget by way of isotopic analyses using a new method of molecular hydrogen recovery and mass spectrometry on sub-liter-sized air samples [*Rahn et al.*, 2002].

2. Site Description: Delta Junction, Alaska

[4] Delta Junction is in the interior of Alaska (lat. 63°48′N, long. 145°06′W, elevation 470 m) in the Yukon-Tanana Uplands on the north eastern flank of the Alaska Range. It is a sub-arctic boreal region with both semi-dry and wet, permafrost-laden soil zones. The area experiences moderate temperatures and precipitation during the summer months (May-August) and exceedingly cold and dry conditions during the winter. Average maximum and minimum annual temperatures between 1937–1999 are 15.6°C (July) and −20°C (January), with annual precipitation of 30 cm falling as rain and 113 cm as snow [*O'Neill*, 2000]. Fire and agriculture are the disturbance regimes that dominate this area, with current fire recurrence intervals averaging 100 years. Black spruce (*Pinus mariana*), feather moss (*Hylocomium*), and cranberry (*Vaccinium macrocarpon*) dominate ecosystems that have not been disturbed by fire within 60 years. Quaking aspen (*Populous tremuloides*), firemoss (*Marchantia polymorpha*), blueberry (*Vaccinium ovaliflorum*), and willow (*Salix* sp.) dominate ecosystems recovering from more recent burns [*Viereck et al.*, 1983]. We chose four sites that represent a chronosequence of ecosystem age after fire: two mixed forests of ages 14 and 45 years (hereafter referred to as sites 87B and 56B, or 'burn' sites) and two mature spruce forests of 140 and 160 years age (sites 94C and 12C, or 'mature' sites). Soil moisture and soil temperature varied with age such that 87B was the driest, warmest site and 12C was the wettest, coolest site. Canopy height in both mature spruce stands was uniform at ~3 to 4 m. The canopy of burn site 87B was open and uneven with maximum aspen height of ~3m and scattered snags and deadfall remaining from the original fire. Burn site 56B was a more developed stand of aspen

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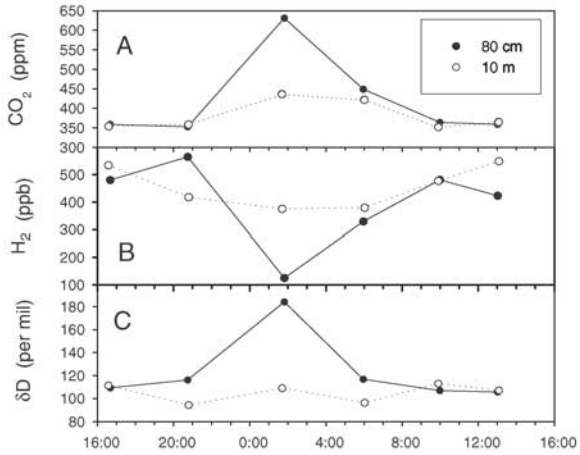

Figure 1. Diel time series collected within (0.8 m) and above (10 m) the forest canopy at burn site 87B. (a) CO_2 concentration (b) H_2 concentration (c) δD of H_2.

with maximum height of ∼5 m and a relatively closed canopy.

3. Sample Collection and Analysis

[5] We collected samples over the course of one week in mid-July of 2001. Flask samples were collected for measurements of atmospheric H_2 concentration ($[H_2]$) and δD during nighttime inversions in the canopies of both mature and burn sites; concurrent sampling of CO_2 concentration ($[CO_2]$) was performed in the field with a LiCor 6200 IR analyzer. Air was pulled from heights of 0 to 2 meters in the forest canopy through double-valve glass flasks of ca. 800 ml volume, and finally into the IR cell of the Licor analyzer. A second set of twelve samples was collected in the same manner over a period of 24 hours at a tower site in a 14 year old mixed forest; in this case, samples were collected at four hour intervals at ground level (0.8 m) and above the canopy (10 m).

[6] Flask samples were analyzed for concentration and δD of H_2 within one month of return to the laboratory using the method of *Rahn et al.* [2002]. Briefly, we condense most components of a whole air sample in a cold trap held at 30 K, leaving only H_2, He, Ne and a small fraction of N_2 as vapor. The non-condensed fraction is then collected on molecular sieve in a valved glass finger at liquid N_2 temperature and removed from the extraction line. It is then connected in line to the He flow at the inlet of a Finnigan Delta Plus XL mass spectrometer where it is focused on an additional molecular sieve trap before entering the mass spectrometer ion source as a single, time resolved peak. The ion beam intensities are compared to those of a reference gas to determine the D/H ratio of the sample. The uncertainty of our isotopic results is ±7‰ [ibid]. In addition, the integrated area of the sample peak is compared to the areas of a series of reference aliquots of known molar quantities, allowing calculation of molarity of the H_2 sample. Given that sample flask volume and pressure are known, this constrains H_2 concentration in the whole air sample. Uncertainty for analysis of H_2 concentration is ∼5% [ibid].

4. Results

4.1. Variability of $[CO_2]$, $[H_2]$, and δD of H_2

[7] The diel variations of $[CO_2]$, $[H_2]$ and δD of H_2 within and above the forest canopy at site 87B from July 18, 1630 hr., to July 19, 1300 hr., are shown in Figure 1. Nighttime highs of $[CO_2]$ reached 635 ppm at 80 cm height at 0149 hr., coincident with an $[H_2]$ minimum of 135 ppb. Above the canopy, $[CO_2]$ was also elevated to >400 ppm during nighttime while $[H_2]$ above canopy was <400 ppb, indicating that nighttime inversion over this period was stable enough to influence even the above-canopy air mass. δD of H_2 at 80 cm was high compared to the average for the whole data base at 0149 hr., coincident with sub-ambient $[H_2]$. Variations in δD of H_2 in the above-canopy air mass is not as apparent. Samples from sites 56B, 94C and 12C were collected within the forest canopy at heights less than 2 m, typically between the hours of 2200 and 0200 and display relationships among $[CO_2]$, $[H_2]$ and δD of H_2 similar to those described for samples collected at night within the canopy at site 87B. Data for samples collected from all sites are combined in Figure 2, although only data for samples collected between 2000 and 0600 hr are included for 87B in order to emphasize samples collected during nighttime inversion conditions.

4.2. H_2 Uptake Rates

[8] Samples collected during nighttime inversions exhibited strong negative correlations between H_2 concentration and CO_2 concentration (Figure 2) with slopes for the burned and mature sites averaging −1.26 and −0.84 ppb H_2 per ppm CO_2, respectively (Table 1). Accumulation of CO_2 in near-surface air masses during nighttime inversions in our study area reflects root and microbial respiration in soils, whereas H_2 uptake by soils under any conditions is believed to be due to abiotic soil hydrogenases [*Conrad et al.*, 1983]. Therefore, the relationship between H_2 and CO_2 observed in our samples likely does not reflect a single chemical or biological reaction (e.g., the metabolism of a single organism). However, the consistent relationship between the two at any one site strongly suggests that they do share a common mechanism for interaction between the biological communities responsible for H_2 consumption and CO_2 production. We propose that this common mechanism is gas exchange between soil and overlying air. Based on this assumption and given known fluxes of CO_2 emission from soils at our study site and the physics of air—soil gas

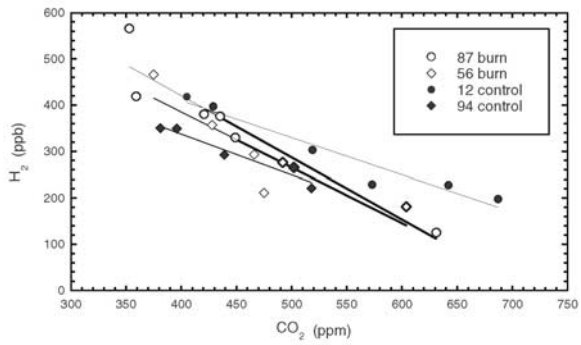

Figure 2. Relationship of H_2 uptake to respired CO_2 observed within the forest canopies during nighttime inversions for the different sites as noted in the legend.

Table 1. Regression analyses of data from Figure 2

Location	R^2	Slope	SE	90% CI
12 control	0.94	−0.80	0.10	−1.02 to −0.59
94 control	0.95	−0.88	0.12	−1.16 to −0.59
87 burn	0.89	−1.34	0.23	−1.83 to −0.84
56 burn	0.78	−1.20	0.31	−1.87 to −0.53

SE=Standard error of slope.
CI=Confidence interval.

exchange, we can use the correlations in Figure 2 to estimate rates of H_2 uptake at our sites.

[9] We estimate the rate of H_2 uptake through the following steps: First, we accept that CO_2 emission from soils in environments and under conditions relevant to our study sites are rate limited either by molecular diffusion (in the case that exchange is rate limited by diffusion through static soil gas) or eddy diffusion (in the case that exchange is rate limited by eddy diffusion in the boundary layer immediately above the soil-atmosphere horizon). In either case, its flux from the soil into overlying air can be described by Fick's first law:

$$F = D\frac{\partial C}{\partial z} \tag{1}$$

where F is the flux (in μmoles m^{-2} s^{-1}), D is the diffusion coefficient (in m^2 s^{-1}), C is the concentration (in μ moles m^{-3}), and z is vertical distance (in m). If we assume that the flux of H_2 into soil is also diffusion limited, and that diffusion coefficients for H_2 and CO_2 are independent of each other, the flux of H_2 can be approximated by the ordinary differential equation:

$$F_{H_2} = F_{CO_2}\left(\frac{D_{H_2}}{D_{CO_2}}\right)\left(\frac{d[H_2]}{d[CO_2]}\right) \tag{2}$$

Thus, we can determine F_{H2} if we know F_{CO2}, the ratios D_{H2}/D_{CO2}, and $d[H_2]/d[CO_2]$. F_{CO2} was measured by flux chamber techniques at or near the sites where the flask samples are collected; over the time period of our study, F_{CO2} in the recently burned, mixed forests averaged 1.4 ± 0.1 μmol m^{-2} s^{-1} and in the mature forest 3.5 ± 0.7 μmol m^{-2} s^{-1}. The relative gradients, $d[H_2]/d[CO_2]$, we take from Figure 2 and Table 1. The ratio of diffusion coefficients for H_2 and CO_2 depends on whether the mixing is via molecular or eddy diffusion. In the case of eddy diffusion, the ratio of diffusion coefficients should be near unity and the H_2 fluxes calculated from Equation 2 would be −1.8 ± 0.5 and −2.9 ± 0.6 nmol m^{-2} s^{-1} at the burned and mature stands respectively. If instead soil gas-atmosphere exchange is rate limited by molecular diffusion in the soil, the ratio of diffusion coefficients will be set by the respective soil gas diffusivities. Soil gas diffusivity is a function of molecular diffusivity in air as well as soil properties and water content. In the case where soils are dry, D_{H2}/D_{CO2} will reduce to the ratio of the respective diffusivities in air. At 20°C, the molecular diffusivities in air of H_2 and CO_2 are 0.627 and 0.160 cm^2 s^{-1}, respectively, yielding a ratio of diffusion coefficients of 3.92. As soils approach saturation, D_{H2}/D_{CO2} will approach the ratio of the respective diffusivities in H_2O. At 20 °C, the molecular diffusivities in H_2O of H_2 and CO_2 are 4.58×10^{-5} and 1.67×10^{-5} cm^2 s^{-1}, respectively, yielding a ratio of diffusion coefficients of 2.74. Diffusion coefficient ratios may approach this saturated case although it should be considered an extreme end member since the absolute values of the diffusion coefficients will essentially lead to a shutdown in soil - atmosphere exchange under fully saturated conditions. H_2 fluxes calculated for the dry soil case are −6.9 ± 2.0 nmol m^{-2} s^{-1} and −12 ± 2.3 nmol m^{-2} s^{-1} for burned and mature forests, respectively and for the saturated soil case are −4.8 ± 1.3 and −7.9 ± 1.6 nmol m^{-2} s^{-1}. The results calculated for the different diffusive regimes are tabulated in Table 2. *Yonemura et al.* [2000b] showed, based on experiments, that variations in soil properties lead to predicted variations in H_2 uptake rates and soil gas diffusivity; given this result and the fact that both respiration of CO_2 and uptake of H_2 take place in the soil column, we conclude that the calculations assuming molecular diffusion as the rate limiting step are the most plausible results.

[10] The destruction rate of trace gases in soils depends on their concentration in overlying air; as a result, rates of gas uptake by soils are commonly reported in terms of deposition velocity (v_d). *Gerst and Quay* [2001] report deposition velocity for H_2 of 0.058 cm s^{-1} in second growth coniferous forest in Seattle, Washington and *Yonemura et al.* [2000a] report v_d of H_2 in a mixed forested area of Japan to be 0.05 to 0.08 cm s^{-1} over a 12 month period. We calculate v_d for the burn and mature forests at our Alaskan sites to be 0.044 ± 0.013 cm s^{-1} and 0.073 ± 0.015 cm s^{-1}, respectively, in the case of molecular diffusion control in dry soil; agreement of these values with previous estimates for similar soil types further supports our preference for the values calculated assuming molecular diffusion is the rate limiting step for soil gas—atmosphere exchange. Deposition velocities of 0.011 ± 0.003 and 0.019 ± 0.004 cm s^{-1} are calculated for the burn and mature sites, respectively, in the alternative case of eddy diffusion control. Previous estimates of deposition velocities for H_2 in other soil types include 0.131 cm s^{-1} in a South African savanna [*Conrad and Seiler*, 1985], 0.010 and 0.016 cm s^{-1} in a South African and Namibian desert soils [ibid], and 0.00 to 0.09 cm s^{-1} in an arable field in Japan; in this last case, deposition velocity decreased with increasing pore water and became negligible in freshly irrigated, saturated soils [*Yonemura et al.*, 1999].

4.3. Isotopic Fractionation During H_2 Soil Uptake

[11] We find that decreasing H_2 concentrations during nighttime inversions are correlated with increasing δD of the remaining H_2 (Figure 3). If we consider this to be a single stage, irreversible loss process, then the fractionation associated with uptake can be estimated by a Rayleigh distillation model. In simplified form, the Rayleigh model can be expressed as

$$\delta D \cong \delta D_o + \varepsilon \times \ln(f) \tag{3}$$

where δD and δD_o are the measured and initial δD values of H_2, 'f' is the fraction of initial H_2 remaining after uptake, and

Table 2. Uptake rates for different diffusivity ratios

Location	$F(D_E)$	$F(D_A)$	$F(D_W)$
12 control	−2.8	−7.6	−11
94 control	−3.1	−8.3	−12
87 burn	−1.9	−5.1	−7.3
56 burn	−1.7	−4.5	−6.6

Fluxes in units of nmol m^{-2} s^{-1}.
Subscripts E, A, and W indicate eddy, air and water diffusivities respectively.

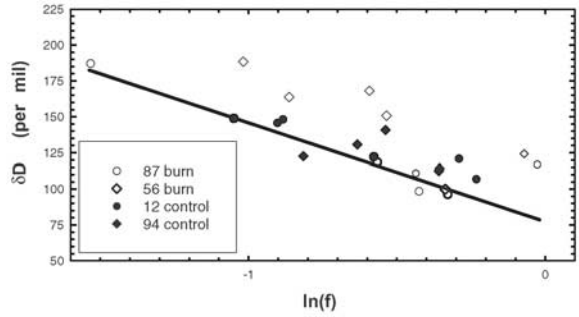

Figure 3. Rayleigh distillation diagram illustrating the isotopic evolution of H_2 in the forest canopy as a function of the natural log of the fraction (f) of H_2 consumed. Sample localities indicated in the legend.

ε is the enrichment factor, which is related to the fractionation factor, α (defined as $D/H_{consumed}/D/H_{residual}$), by the equation $\varepsilon = 1000\cdot(\alpha - 1)$. Based on linear regressions of data for each of the individual sites in Figure 3, we find $\varepsilon = -74.5 \pm 15‰$ ($R^2 = 0.79$) and $-78.0 \pm 26‰$ ($R^2 = 0.70$) for burn sites 87B and 56B and $\varepsilon = -27.0 \pm 31‰$ ($R^2 = 0.20$) to $-49.7 \pm 7.6‰$ ($R^2 = 0.91$) for mature sites 12C and 94C. The calculated fractionation factor associated with uptake appears to be greater for burned vs. mature sites, perhaps indicating that low uptake rates involve greater isotopic fractionation than fast uptake rates. However, the standard deviations of regressions for each site in Figure 3 are large enough that this result, though suggestive, cannot be considered statistically significant. If data for all sites are regressed together, we find $\varepsilon = -59 \pm 11‰$ ($R^2 = 0.59$), comparable to the values of $-57 \pm 24‰$ reported by *Gerst and Quay* [2001] and $-60‰$ reported by *Ehhalt* [1989].

5. Discussion

[12] We draw several general conclusions based on our observations of H_2 and δD of H_2 in the boreal forest system of interior Alaska. First, H_2 levels during nighttime inversions within boreal forest canopies fell to as low as 25% of the average tropospheric concentration indicating that these ecosystems act as net sinks of atmospheric H_2. Furthermore, correlation of H_2 with respired CO_2 in these canopies provides us with the means to interpret the results in terms of net flux with rates that are comparable to those previously determined for soils in temperate and tropical regions, whether eddy diffusivity or molecular diffusivity is the controlling factor. Finally, the data in Table 2 suggest that there may be observable differences in the rate of uptake between young mixed forests and mature stands. Given that fire frequency may increase with increasing average temperatures and changing land-use patterns in boreal regions [*Kasischke et al.*, 1995], our results suggest that the capacity for H_2 soil uptake may be modified in the future.

[13] The cause of the difference in rate of H_2 uptake between recently burned and mature forests could have several explanations. We note *Conrad and Seiler* [1985] found H_2 deposition velocities are positively correlated with soil organic carbon. Total carbon in soils from our 'mature' sites averages 217 Mg ha^{-1} whereas that in our 'burned' sites averages 177 Mg ha^{-1} [*O'Neill*, 2000]. Furthermore, 70% of the carbon in the mature sites near Delta Junction is in the organic horizon, whereas 92% of carbon in recently burned sites is in the mineral horizon and may have a significant contribution of inorganic carbon. Thus, recent burn sites have systematically lower soil organic carbon inventories than mature sites and would therefore be predicted to have lower deposition velocities for H_2, all other parameters being equal. On the other hand, mature spruce stands typically retain more soil moisture which would tend to reduce the H_2 uptake at these sites. The true variability between and within these sites will require more detailed future field studies investigating additional influencing components of the ecosystems such as the potential for in situ production of H_2 via nitrogen fixation.

[14] The isotopic fractionations associated with uptake of H_2 in both 'burned' and 'mature' forests in this study are comparable to those observed in previous studies of mid-latitude forests and cultivated grass [*Ehhalt et al.*, 1989; *Gerst and Quay*, 2001]. This similarity across ecosystems and between flux chamber experiments and our field study suggests that the common value of ε observed in these studies (ca. $-60‰$) is a reasonable choice for modeling the role of soil uptake in the global isotopic budget of H_2. However, we re-iterate that our results suggest variability in ε that should be examined with more detailed study covering a wider range of ecosystems.

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